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2-Cyanoanilinium iodide

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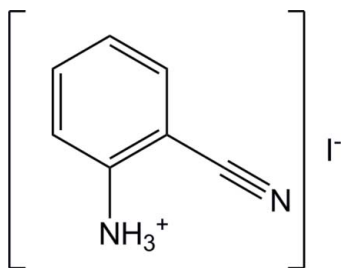
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.016; wR factor = 0.041; data-to-parameter ratio = 23.0.

The solid-state structure of the title salt, $\text{C}_7\text{H}_7\text{N}_2^+\text{I}^-$, consists of cation–anion sheets lying parallel to (110), with the components linked by $\text{N}-\text{H}\cdots\text{I}$ hydrogen bonds.

Related literature

For the structure of 2-cyano-1-methylpyridinium iodide, see: Kammer *et al.* (2013). For structures of other 2-cyanoanilinium salts, see: Cui & Chen (2010); Zhang (2009); Cui & Wen (2008); Oueslati *et al.* (2005). For the structures of 4-cyanoanilinium halides, see: Mague *et al.* (2012); Vumbaco *et al.* (2012); Colapietro *et al.* (1981).



Experimental

Crystal data

 $\text{C}_7\text{H}_7\text{N}_2^+\text{I}^-$ $M_r = 246.05$ Orthorhombic, $Pbca$ $a = 10.1474$ (15) Å $b = 8.6979$ (13) Å $c = 18.073$ (3) Å $V = 1595.2$ (4) Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 3.94$ mm⁻¹ $T = 100$ K $0.20 \times 0.19 \times 0.16$ mm

Data collection

Bruker SMART APEX CCD diffractometer

Absorption correction: numerical (*SADABS*; Bruker, 2010) $T_{\min} = 0.43$, $T_{\max} = 0.58$

25911 measured reflections

2112 independent reflections

2030 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.039$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.016$ $wR(F^2) = 0.041$ $S = 1.10$

2112 reflections

92 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.59$ e Å⁻³ $\Delta\rho_{\min} = -0.58$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{I1}$	0.88	2.74	3.6069 (13)	169
$\text{N1}-\text{H1B}\cdots\text{I1}^{\text{i}}$	0.88	2.71	3.5501 (14)	160
$\text{N1}-\text{H1C}\cdots\text{I1}^{\text{ii}}$	0.88	2.84	3.6615 (13)	156

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, z$.

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXM* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7106).

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supplementary materials

Acta Cryst. (2013). E69, o1288 [doi:10.1107/S1600536813019314]

2-Cyanoanilinium iodide

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Comment

In the solid state, salts of the isomeric cyanoanilinium ions exhibit both layer and network structures. Thus, the iodide (Mague *et al.*, 2012) and chloride (Colapietro *et al.*, 1981) salts of the 4-cyanoanilinium ion as well as the chloride (Oueslati, *et al.*, 2005) and nitrate (Cui & Wen, 2008) salts of the 2-cyanoanilinium ion have layer structures in which the -NH_3^+ and anion moieties form a double layer with the organic portion of the cations protruding perpendicularly from both sides of this double layer. By contrast, the bromide (Zhang, 2009) and perchlorate (Cui & Chen, 2010) salts of the 2-cyanoanilinium ion form network structures while 4-cyanoanilinium bromide (Vumbaco *et al.*, 2012) forms a stepped layer structure. A different structure type is found in the title compound where the basic unit is a zigzag chain of alternating cations and anions running parallel to *a* assembled by alternating short and long $\text{N-H}\cdots\text{I}$ hydrogen bonds (Table 1, Fig. 1). These chains are assembled into sheets parallel to (110) by intermediate length $\text{N-H}\cdots\text{I}$ hydrogen bonds between cations in one chain and anions in the next in which the cations in each chain are arranged in an "umbrella" fashion (Fig. 3) instead of projecting straight out towards the edges of the layer. It is also significantly different from the structure adopted by the isomeric compound 2-cyano-*N*-methylpyridinium iodide (Kammer *et al.*, 2013), at least in part because the intermolecular $\text{C-H}\cdots\text{I}$ interactions in this compound are expected to be weaker than the $\text{N-H}\cdots\text{I}$ interactions in the title compound.

Experimental

2-Cyanoaniline (0.55 g) and 1.0 ml of aqueous hydroiodic acid (47% by mass) were combined in 10 ml of ethanol. This solution was slowly evaporated to dryness at room temperature to form colourless blocks of the title compound.

Refinement

H-atoms attached to carbon were placed in calculated positions ($\text{C-H} = 0.95 \text{ \AA}$) while those attached to nitrogen were placed in locations derived from a difference map and their coordinates then adjusted to give $\text{N-H} = 0.88 \text{ \AA}$. All were included as riding contributions with isotropic displacement parameters 1.2 times those of the attached atoms.

Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT* (Bruker, 2010); program(s) used to solve structure: *SHELXM* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

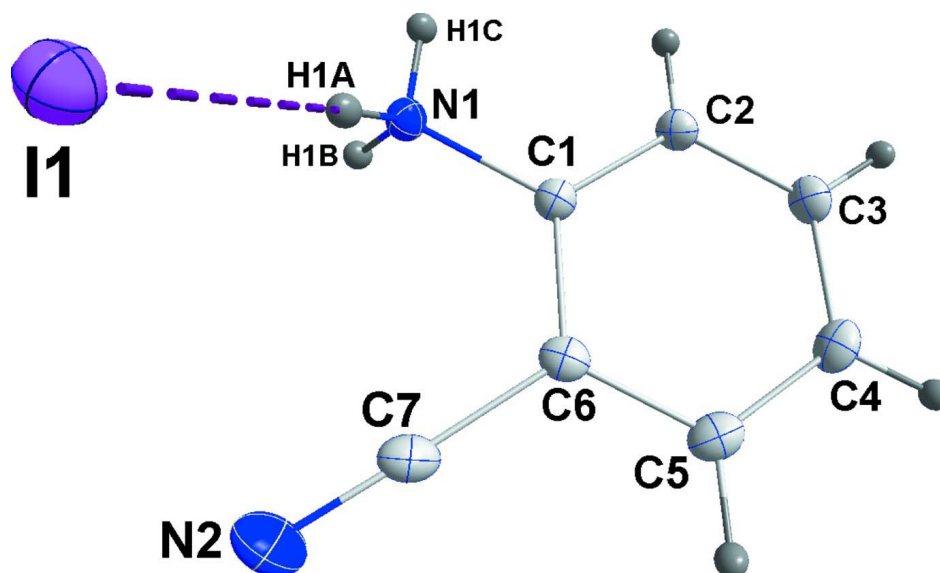


Figure 1

Perspective view of the cation–anion pair showing the shortest interionic N—H...I hydrogen bonds and 50% probability displacement ellipsoids.

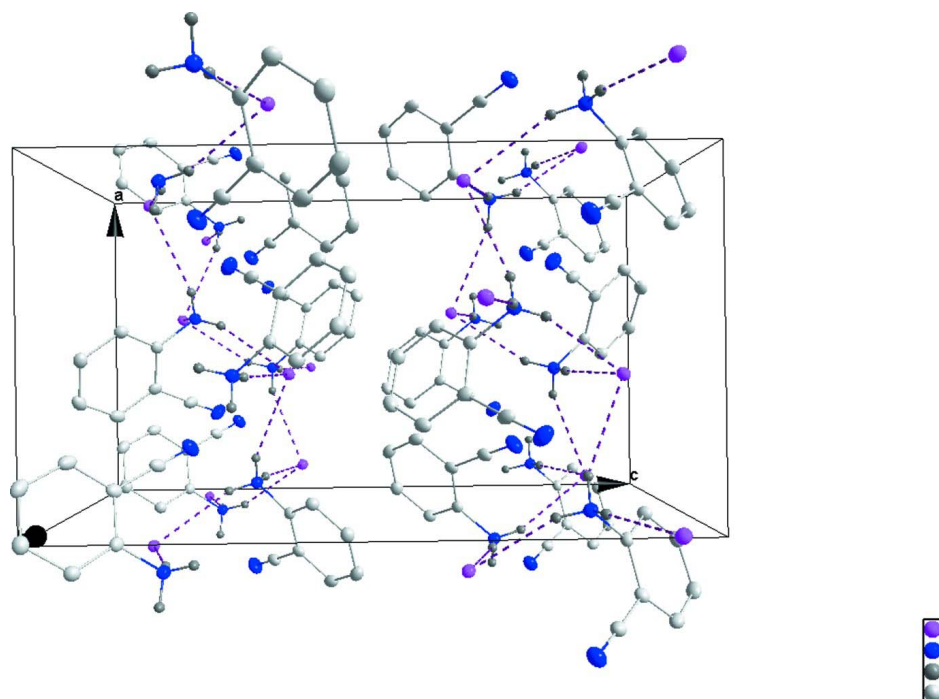
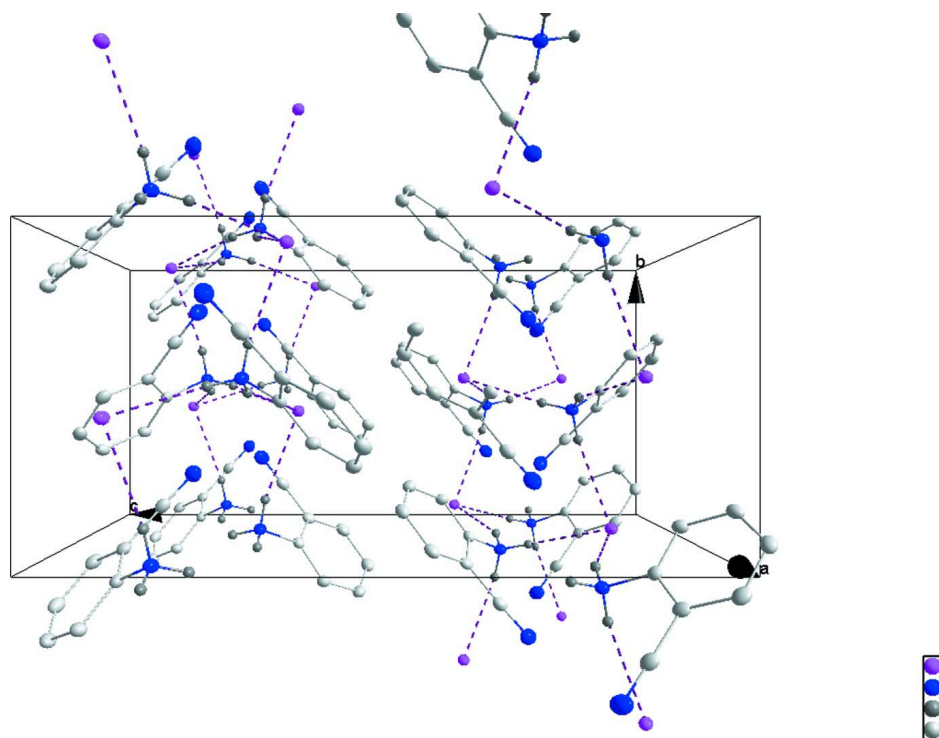


Figure 2

Packing viewed down the *b* axis with N—H...I interactions shown as dotted lines.

**Figure 3**

Packing viewed down the *a* axis with N—H...I interactions shown as dotted lines.

2-Cyanoanilinium iodide

Crystal data

$C_7H_7N_2^+I^-$

$M_r = 246.05$

Orthorhombic, *Pbca*

$a = 10.1474 (15) \text{ \AA}$

$b = 8.6979 (13) \text{ \AA}$

$c = 18.073 (3) \text{ \AA}$

$V = 1595.2 (4) \text{ \AA}^3$

$Z = 8$

$F(000) = 928$

$D_x = 2.049 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 9853 reflections

$\theta = 2.3\text{--}29.1^\circ$

$\mu = 3.94 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, colourless

$0.20 \times 0.19 \times 0.16 \text{ mm}$

Data collection

Bruker SMART APEX CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $8.3660 \text{ pixels mm}^{-1}$

φ and ω scans

Absorption correction: numerical

(*SADABS*; Bruker, 2010)

$T_{\min} = 0.43$, $T_{\max} = 0.58$

25911 measured reflections

2112 independent reflections

2030 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 29.1^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -13 \rightarrow 13$

$k = -11 \rightarrow 11$

$l = -24 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.016$
 $wR(F^2) = 0.041$
 $S = 1.10$

2112 reflections

92 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 0.7585P]$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.59 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.58 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL2013* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00151 (13)

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω , collected at $\varphi = 0.00, 90.00$ and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ , collected at $\omega = -30.00$ and 210.00° . The scan time was 10 sec/frame.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.58823 (2)	0.05477 (2)	0.13679 (2)	0.01326 (5)
N1	0.58054 (12)	0.44877 (14)	0.19889 (8)	0.0140 (3)
H1A	0.5870	0.3496	0.1900	0.017*
H1B	0.5590	0.4716	0.2448	0.017*
H1C	0.6593	0.4909	0.1973	0.017*
N2	0.28338 (14)	0.23930 (17)	0.21818 (8)	0.0246 (3)
C1	0.49549 (15)	0.51204 (18)	0.14089 (7)	0.0129 (3)
C2	0.54089 (14)	0.63213 (16)	0.09804 (8)	0.0149 (3)
H2	0.6252	0.6758	0.1071	0.018*
C3	0.46120 (15)	0.68861 (17)	0.04120 (8)	0.0170 (3)
H3	0.4916	0.7711	0.0113	0.020*
C4	0.33787 (15)	0.62516 (17)	0.02809 (8)	0.0183 (3)
H4	0.2854	0.6627	-0.0115	0.022*
C5	0.29073 (15)	0.50692 (19)	0.07257 (8)	0.0172 (3)
H5	0.2054	0.4654	0.0643	0.021*
C6	0.36974 (17)	0.44965 (16)	0.12950 (8)	0.0141 (3)
C7	0.32073 (14)	0.33165 (17)	0.17807 (8)	0.0167 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01359 (7)	0.01201 (7)	0.01419 (7)	-0.00040 (3)	-0.00112 (3)	-0.00004 (3)
N1	0.0147 (6)	0.0120 (6)	0.0152 (6)	-0.0004 (4)	-0.0008 (4)	0.0005 (4)
N2	0.0270 (7)	0.0236 (7)	0.0233 (7)	-0.0071 (6)	0.0076 (6)	-0.0023 (6)
C1	0.0145 (7)	0.0117 (7)	0.0126 (6)	0.0012 (5)	0.0003 (5)	-0.0022 (5)

C2	0.0153 (6)	0.0120 (6)	0.0174 (6)	−0.0003 (5)	0.0003 (5)	−0.0002 (5)
C3	0.0210 (7)	0.0127 (7)	0.0174 (7)	0.0019 (6)	0.0010 (5)	0.0009 (5)
C4	0.0213 (7)	0.0163 (7)	0.0174 (6)	0.0050 (6)	−0.0035 (5)	−0.0020 (6)
C5	0.0150 (6)	0.0166 (7)	0.0199 (7)	0.0020 (6)	−0.0011 (5)	−0.0058 (6)
C6	0.0142 (8)	0.0119 (7)	0.0161 (7)	0.0012 (5)	0.0029 (5)	−0.0033 (5)
C7	0.0143 (6)	0.0174 (7)	0.0182 (7)	−0.0017 (5)	0.0023 (5)	−0.0053 (6)

Geometric parameters (Å, °)

N1—C1	1.4651 (19)	C2—H2	0.9500
N1—H1A	0.8800	C3—C4	1.388 (2)
N1—H1B	0.8800	C3—H3	0.9500
N1—H1C	0.8800	C4—C5	1.390 (2)
N2—C7	1.146 (2)	C4—H4	0.9500
C1—C2	1.380 (2)	C5—C6	1.396 (2)
C1—C6	1.402 (2)	C5—H5	0.9500
C2—C3	1.397 (2)	C6—C7	1.439 (2)
C1—N1—H1A	106.4	C4—C3—H3	119.7
C1—N1—H1B	116.3	C2—C3—H3	119.7
H1A—N1—H1B	114.3	C3—C4—C5	120.37 (14)
C1—N1—H1C	110.8	C3—C4—H4	119.8
H1A—N1—H1C	109.6	C5—C4—H4	119.8
H1B—N1—H1C	99.3	C4—C5—C6	119.51 (14)
C2—C1—C6	120.98 (13)	C4—C5—H5	120.2
C2—C1—N1	119.30 (13)	C6—C5—H5	120.2
C6—C1—N1	119.72 (13)	C5—C6—C1	119.52 (14)
C1—C2—C3	119.07 (14)	C5—C6—C7	120.37 (15)
C1—C2—H2	120.5	C1—C6—C7	120.07 (14)
C3—C2—H2	120.5	N2—C7—C6	178.30 (17)
C4—C3—C2	120.51 (14)		
C6—C1—C2—C3	−1.9 (2)	C4—C5—C6—C7	177.45 (14)
N1—C1—C2—C3	177.87 (13)	C2—C1—C6—C5	1.9 (2)
C1—C2—C3—C4	0.2 (2)	N1—C1—C6—C5	−177.89 (13)
C2—C3—C4—C5	1.6 (2)	C2—C1—C6—C7	−175.70 (13)
C3—C4—C5—C6	−1.6 (2)	N1—C1—C6—C7	4.5 (2)
C4—C5—C6—C1	−0.1 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots I1	0.88	2.74	3.6069 (13)	169
N1—H1B \cdots I1 ⁱ	0.88	2.71	3.5501 (14)	160
N1—H1C \cdots I1 ⁱⁱ	0.88	2.84	3.6615 (13)	156

Symmetry codes: (i) $-x+1, y+1/2, -z+1/2$; (ii) $-x+3/2, y+1/2, z$.